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COMMUNICATION

Halogenation of A-Frame μ-Carbido Complexes: Synthesis of μ_2-Halocarbynes

Harrison J. Barnett[a] and Anthony F. Hill[*,a]

The reaction of $[Rh_2(\mu\text{-}C)Cl_2(PPh_3)_4]$ with bis(diphenylphosphino)methane (dppm) affords the A-frame μ-carbido complex $[Rh_2(\mu\text{-}C)Cl_2(\mu\text{-}dppm)_2]$, halide metathesis of which provides $[Rh_2(\mu\text{-}C)Br_2(\mu\text{-}dppm)_2]$. The reactions of the former with $PhICl_2$ or the latter with $[pyH][Br_3]$ provide rare examples of μ_2-halocarbyne ligands in the complexes $[Rh_2(\mu\text{-}CX)(\mu\text{-}X)X_4(\mu\text{-}dppm)_2]$ (X = Cl, Br).

Linear bimetallic μ-carbido complexes may be described by one of three distinct bonding modes (Chart 1) depending on the effective atomic number requirements of the metal termini. The simplest and oldest[1] involve identical metal termini and are best described as dimetallacumulenic in nature (Class **A**, Chart 1) with two formal M=C double bonds.

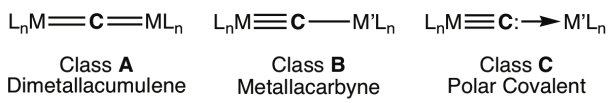
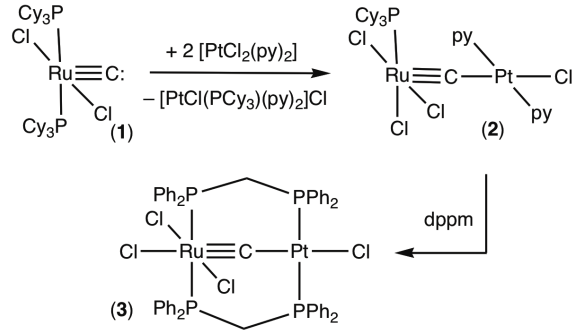


Chart 1. Distinct μ-Carbido Bonding Modes.[1-4]

When the two metal termini differ, the possibility of distinct metal-carbon single and triple bonds arises[2] such that a metallacarbyne description is more appropriate (Class **B**, Chart 1). Carbido complexes of this form in most cases arise from reactions of halo-, seleno- or lithiocarbyne reagents $[M(\equiv CA)(CO)_2(Tp^*)]$ (A = Br, Cl, Li, Se^-; Tp* = hydrotris(dimethylpyrazolyl)borate). The first example $[WRu(\mu\text{-}C)(O^tBu)_3(CO)_2(\eta\text{-}C_5H_5)]$ was reported by Selegue,[2a] however, to result from an alkyne metathesis reaction involving C≡C scission of the ruthenium propynyl complex $[Ru(C{\equiv}CMe)(CO)_2(\eta\text{-}C_5H_5)]$. Class **B** μ-carbido complex have been implicated in palladium-mediated catalytic C–C and C–P bond forming reactions of bromocarbynes.[3] The third class (**C**) involve a polar-covalent (dative) coordination of the terminal carbido complex $[Ru(C)Cl_2(PCy_3)_2]$ (**1**)[4] to a wide variety of metal centres,[4,5] in a manner akin to σ-donor/π-acidic CO and isonitrile ligands.[5] It was recently demonstrated that one such Class **B** μ-carbido complex, $[RuPt(\mu\text{-}C)Cl_4(py)_2(PCy_3)]$ (**2**),[4d] which is obtained from **1** and *trans*-$[PtCl_2(py)_2]$ presumably *via* Class **C** $[RuPt(\mu\text{-}C)Cl_4(py)_2(PCy_3)_2]$, reacted with bis(diphenylphosphino)-methane (dppm) to afford the first example of an 'A-frame'[6] μ-carbido complex $[RuPt(\mu\text{-}C)Cl_4(dppm)_2]$ (**3**) in which the octahedral d^6-ruthenium(II) and square planar d^8-platinum(II) centres,[7] respectively form triple and single bonds to the bridging carbido ligand (Scheme 1). This sequence constituted the first demonstration of the interconversion of two classes of μ-carbido complex (**C** → **B**).



Scheme 1. Synthesis of a Class **B** 'A-Frame' μ-Carbido complex.[4d]

The advent of the readily accessible symmetrical class **A** carbido complex $[Rh_2(\mu\text{-}C)Cl_2(PPh_3)_4]$ (**4**)[8] suggested to us the possibility of exploring not only *symmetrical* Class **A** A-frame μ-carbido complexes but also the interconversion of carbido classes by exploiting the synthetic versatility typical of square planar d^8-rhodium centres. We report herein both endeavours, the first of which proceeded without issue, whilst the latter afforded unprecedented access to the first examples of μ_2-CCl and μ_2-CBr ligands.

Treating a suspension of **4** in benzene with dppm results in clean conversion to provide the A-frame complex $[Rh_2(\mu\text{-}C)Cl_2(\mu\text{-}dppm)_2]$ (**5a**) in 97% yield. The characterisation of **5a** (see ESI) included a crystallographic analysis, the results of which are summarised in Figure 1a along with those for the crystallographically centrosymmetric ($P2_1/c$) salt

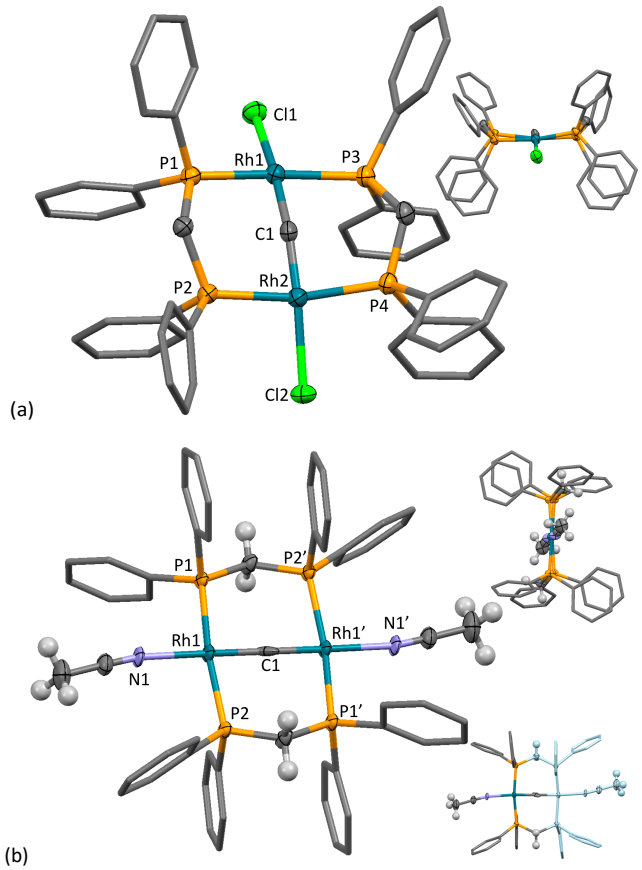
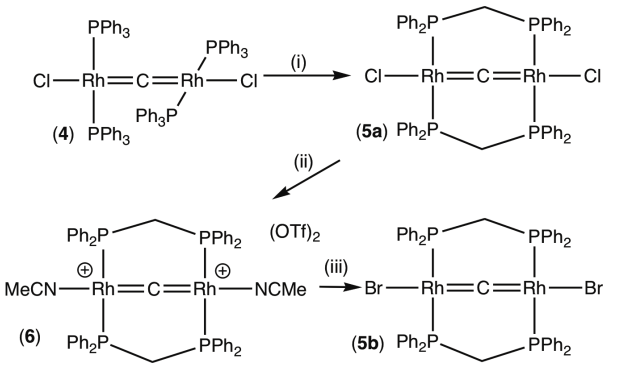


Figure 1. Molecular structures of A-Frame μ-Carbido Complexes (50% displacement ellipsoids, solvent, counter anion and hydrogen atoms omitted, phenyl groups simplified) **5a** (in a crystal of **5a**.$2CH_2Cl_2$) and **6** (in a crystal of **6**.C_6H_5Me, only half the molecule is crystallographically unique due to an inversion centre at C1) . Selected bond lengths (Å) and angles (°): (a) **5a**: Rh1-C1 1.732(11), Rh2-C1 1.757(11), Rh1-P3 2.328(3), Rh1-Cl1 2.418(3), Rh1-C1-Rh2 162.6(7), C1-Rh1-P3 84.6(3) (b) **6**: Rh1-C1 1.7443(5), Rh1-N1 2.167(7), Rh1-P1 2.324(2), Rh1-C1-Rh1′ 180.0(0), N1-Rh1-C1 173.6(2). Insets show views along inter-rhodium vector and symmetry-generated (pale blue) half of **6**.

$[Rh_2(\mu\text{-}C)(NCMe)_2(\mu\text{-}dppm)_2](OTf)_2$ (**6**, Figure 1b) which is readily obtained from **5a** and AgOTf in acetonitrile (Scheme 2).

Other than confirming the equivalence of Rh=C bonding in the symmetric Class **A** coordination mode, the most notable structural feature of both **5a** and **6** is that the two rhodium coordination planes approach coplanarity with P-Rh···Rh-P torsional angles close to zero (**5a**:7.55, 7.36; **6**: 7.25, °). This is in contrast to the precursor **4** in which the two rhodium coordination planes are approximately orthogonal so as to minimise steric repulsion between (unlinked) phosphines on adjacent rhodium centres. In the absence of ^{13}C enrichment[8] the identification and resolution of the 15 line multiplets expected for the quaternary μ-carbido nuclei in the $^{13}C\{^1H\}$ NMR spectra of either **5a** and **6** was not viable (coupling to ^{31}P and



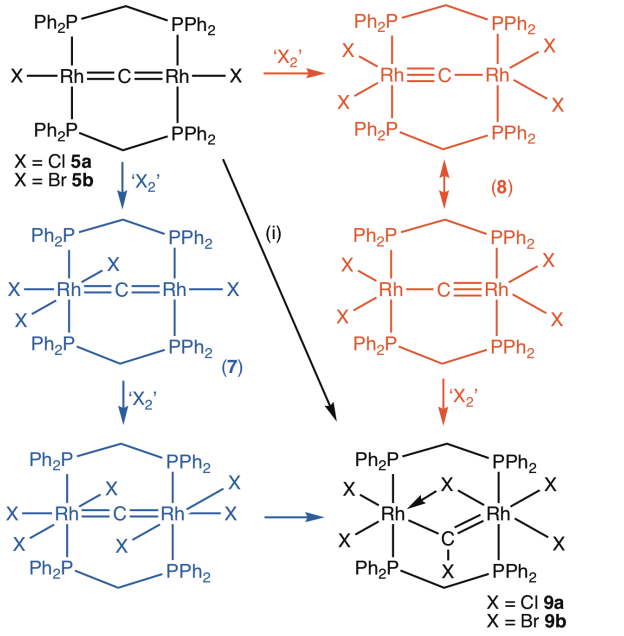
Scheme 2. Synthesis of Class **A** 'A-Frame' μ-carbido complexes. (i) dppm, (ii) AgOTf, MeCN, (iii) KBr.

^{103}Rh), however all other spectroscopic, elemental microanalytical and MS data were consistent with the formulations.

The predilection of square-planar d^8-Rh(I) complexes towards oxidative addition underpins a multitude of catalytic processes. In the present context, the possibility that redox processes at rhodium might be accompanied by changes in the character (**A**, **B** or **C**) of the bridging carbido ligand appeared attractive given the intrinsically robust nature of the A-frame platform which has been shown to support many ligand transformations without rupture.[6c] For simplicity, we chose simple chlorination, anticipating two possible outcomes depending on whether 1,1 or 1,3 addition of *one equivalent* of Cl_2 to the complex ensued (Scheme 2). The former would be expected to provide complex **7** featuring a Class **A** Rh^{III}=C=Rh^{I} connectivity, a single example of which $[Rh_2(\mu\text{-}C)(\mu\text{-}C_6H_4PPh_2\text{-}2)H(Tp^*)_2]$ (Tp* = hydrotris(dimethylpyrazoyl)borate) has been recently reported.[8] Conversely, 1,3 addition might provide a symmetrical μ-carbido complex **8**, for which two degenerate Class **B** canonical descriptors would be required.

Elemental chlorine proved too vigorous a chlorinating reagent, however $PhICl_2$ cleanly served our purposes. It however transpired that no product of mono-addition of Cl_2 could be readily isolated and a clean high-yielding process could only be achieved by addition of two or more equivalents of $PhICl_2$. Whilst either **7** or **8** are plausible intermediates, the product isolated was formulated as the first example of a μ_2-chlorocarbyne complex $[Rh(\mu\text{-}CCl)(\mu\text{-}Cl)Cl_4(\mu\text{-}dppm)_2]$ (**9a**). The corresponding per-brominated example $[Rh(\mu\text{-}CBr)(\mu\text{-}Br)Br_4(\mu\text{-}dppm)_2]$ (**9b**) could be obtained *via* the sequential treatment of **6** with potassium bromide to afford the neutral complex $[Rh_2(\mu\text{-}C)Br_2(\mu\text{-}dppm)_2]$ (**5b**) followed by pyridinium tribromide (Scheme 3).

The C_{2v}-symmetric natures of **9a** and **9b** were confirmed by the appearance of simple doublet resonances in the $^{31}P\{^1H\}$ NMR spectra moved to lower frequency of the precursor (δ_P = 3.38 **9a**; –5.73 **9b**) and displaying $^1J_{PRh}$ couplings the magnitudes of which (95 **9a**, 96 **9b** Hz) are consistent with six-coordinate rhodium centres (*cf.* 191 Hz for 4-cooordinate **5a**). Consideration together of the infrared spectra for both **9a** and **9b** allows by a process of elimination, the identification of the ν_{CCl} absorption in the former at 852 cm^{-1}. For reasons noted



Scheme 3. Halogenation of a bridging carbido ligand. (i) 2 $PhICl_2$ (X = Cl) or 2 $[pyH][Br_3]$ (X = Br); proposed intermediate complexes depicted in red or blue were not observed.

above, the expected triple pentet resonances for the bridging carbyne carbon nuclei were not identified in the $^{13}C\{^1H\}$ NMR spectra. The characterisation of both **9a** and **9b**, however, included crystallographic analyses (Figure 2).

The crystallographic data confirmed the approximately C_{2v} symmetric nature of **9a** and crystallographically imposed C_2 symmetry of **9b**, in addition to the presence of the μ_2-CX ligands. For these, the C–X vectors are orthogonal (89.99° **9a**, 90.00° **9b**) to their respective Rh···Rh vectors which we eschew describing as bonds (3.1866(7) **9a**, 3.220(3) **9b** Å). Despite their proximity, the effective atomic number requirements of the rhodium centres do not call for the invocation of metal-metal bonding, as coordinative saturation is satisfied by the degenerate valence bond description shown in Scheme 3. Structural data are only available for a single example of a dirhodium μ-carbyne complex, $[Rh_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(\eta\text{-}C_5Me_5)_2]BPh_4$,[9] which has a mean Rh–C separation of 1.903(10) Å across what must be described as a Rh–Rh bond (2.568(1)Å) of multiple character ($2r_{cov}$(Rh) = 2.96 Å). Whilst μ_3-halocarbyne complexes are common and date back almost 60 years to the discovery of $[Co_3(\mu\text{-}CCl)(CO)_9]$,[10] terminal halocarbynes are somewhat rare.[11] Bimetallic μ-halocarbyne complexes are limited to the report of a single complex $[MoPt(\mu\text{-}CBr)(CO)_2(PPh_3)_2(Tp^*)]$ spectroscopically observed by Beck *en route, via* C–Br oxidative addition, to the Class **B** μ-carbido $[MoPt(\mu\text{-}C)Br(CO)_2(PPh_3)_2(Tp^*)]$.[12] The complexes **9** therefore provide the first structural data for μ_2-halocarbynes. Taken together, the dimensions of the $Rh_2\mu$-C core are rather similar with almost identical Rh···Rh separations (difference = 0.0334 Å, 11 e.s.d.) consistent with their proximity being dictated by the geometric constraints of four bridging ligands rather than any significant inter-metallic bonding. The Rh–C bonding is significantly shorter (0.112 Å, 28 e.s.d.) in **9a** than in **9b**, which is consistent with the

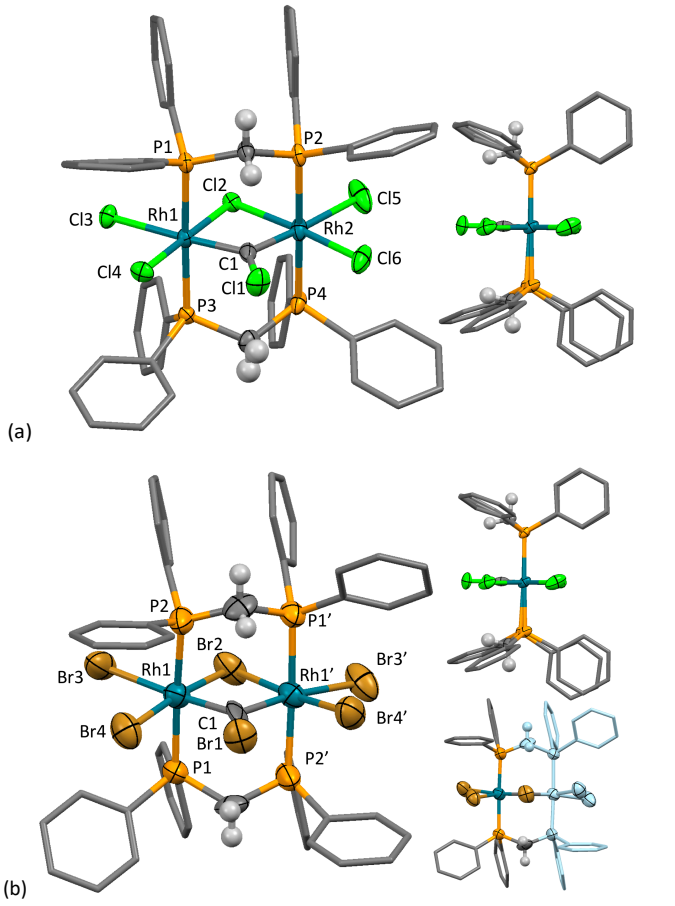


Figure 2. Molecular structures of (a) **9a** in a crystal of **9a**.$CHCl_3$, (b) **9b** (one half of the molecule is crystallographically unique due to a 2 axis passing through Br2, C1 and Br1) (50% displacement ellipsoids, hydrogen atoms omitted, phenyl groups simplified). Selected bond lengths (Å) and angles (°) for **9a**: Rh1···Rh2 3.1866(7), Rh2-C1 1.948(6), Rh2-C1 1.912(6), C1-Cl1 1.674(7), Rh1-Cl2 2.403(1), Rh1-P1 2.381(2), Cl1-H91A 2.983, Rh1-C1-Rh2 111.3(3), C1-Rh1-Cl2 83.0(2). **9b**: Rh1-C1 2.09(4), C1-Br1 1.60(6), Rh1···Rh1' 3.220(3), Rh1-Br2 2.494(4), Rh1-P1 2.382(7), Rh1-Br4 2.458(5), Rh1-C1-Rh1' 103(2), Br2-Rh1-C1 88.5(13). Insets show views along Rh···Rh inter-rhodium vectors and symmetry generated (pale blue) half of **9b**.

bromide being a more effective π-donor to trigonal carbon than is chloride,[13] somewhat diminishing retrodonation from rhodium to carbon. A feature common to both structures is the close approach of one proton of each dppm methylene group to the halocarbyne carbon. The ^1H NMR spectra of both complexes display quite different chemical shifts for the diastereotopic methylene protons, *e.g.,* δ_H = 3.56 and 3.20 for **9a**, suggesting perhaps that this association persists to some extent in solution. It may, however be a simple geometric corollary of the necessary folding of the Rh_2P_2C envelope. The halocarbyne ligand in each case exerts a most pronounced *trans* influence relative to the bridging halide.

In conclusion, although oxidative interconversion of carbido bonding classes was not in this instance demonstrated, the chemically robust nature of the A-frame assembly did allow chemical modification of the carbido ligand, converting it to novel chloro- and bromocarbyne bridges, the pronounced *trans* influence of which could be demonstrated. Although the number of linear μ_2-carbido complexes continues to grow, actual examples of their carbido-based reactivity remain rare,

being limited to oxidation to a carbonyl ligand,[8] protonation,[2b] insertion of CS_2[2b] and phosphine coupling[2c] in addition to the reductive elimination processes implicit in their involvement in palladium mediated C–C and C–P bond formation.[3] We anticipate that A-frame carbido complexes such as **3**, **5** and **6** should provide a suitably sturdy platform for exploring ligand-based μ-carbido reactivity and intermetallic communication.

Acknowledgements

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